

## WHAT IS CLAIMED IS:

1. A catalyst for use in producing a lower aliphatic carboxylic acid ester, which is used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

### First Step

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

### Second step

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

2. The catalyst as claimed in claim 1, wherein the second step is performed in the reactor used in reacting the lower olefin with the lower aliphatic carboxylic acid in a gas phase.

3. The catalyst as claimed in claim 1 or 2, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

4. A process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, said catalyst being used in reacting a lower olefin with a lower aliphatic

carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

**First Step**

a step for loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

**Second Step**

a step for contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester.

5. The process as claimed in claim 4, wherein the second step is performed in the reactor used in reacting the lower olefin with the lower aliphatic carboxylic acid in a gas phase.

6. The process as claimed in claim 4 or 5, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

7. The process as claimed in any one of claims 4 or 5, wherein the second step is performed at a temperature of 80 to 300°C.

8. The process as claimed in any one of claims 4 or 5, wherein the second step is performed under a pressure of 0 to 3 MPaG (gauge pressure).

9. The process as claimed in any one of claims 4 or 5, wherein the second step is performed at a gas hourly space velocity (GHSV) of 100 to 7,000 hr<sup>-1</sup>.

10. The process as claimed in any one of claims 4 or 5, wherein the gas containing

at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols used in the second step is a mixed gas of water and acetic acid.

11. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of the catalyst as claimed in any one of claims 1 or 2.

12. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of water and the catalyst as claimed in any one of claims 1 or 2.

13. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which process comprises the following first to fourth steps:

First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst;

Second Step

a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in the reaction of the lower olefin with the lower aliphatic carboxylic acid in a gas phase;

Third Step

a step of contacting the heteropolyacid salt supported catalyst filled in the reactor, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols; and

Fourth Step

a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester.

14. The process as claimed in claim 13, wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

15. The process as claimed in claim 13 or 14, wherein the third step is performed at a temperature of 80 to 300°C.

16. The process as claimed in any one of claims 13 or 14, wherein the third step is performed under a pressure of 0 to 3 MPaG (gauge pressure).

17. The process as claimed in any one of claims 13 or 14, wherein the third step is performed at a gaseous hourly space velocity (GHSV) of 100 to 7,000 hr<sup>-1</sup>.

18. The process as claimed in any one of claims 13 or 14, wherein the lower aliphatic carboxylic acid used in the third step is the same as the lower aliphatic carboxylic acid used in producing the lower aliphatic carboxylic acid ester.

19. The process as claimed in any one of claims 13 or 14, wherein the mixed gas containing a lower olefin and a lower aliphatic carboxylic acid used in the fourth step contains water.

20. A catalyst for use in producing a lower aliphatic carboxylic acid ester, which is used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, wherein the catalyst is produced by a process comprising the following first and second steps:

First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step of contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, in the absence of any lower olefin, to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester;

wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

21. A process for producing a catalyst for use in producing a lower aliphatic carboxylic acid ester, said catalyst being used in reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase to produce a lower aliphatic carboxylic acid ester, which process comprises the following first and second steps:

First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst; and

Second Step

a step of contacting the heteropolyacid salt supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, in the absence of any lower olefin, to obtain the catalyst for use in producing a lower aliphatic carboxylic acid ester;

wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, silicomolybdic acid, silicovanadotungstic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

22. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which process comprises the following first to fourth steps:

First Step

a step of loading one or more heteropolyacid salts on a support to obtain a heteropolyacid salt supported catalyst;

Second Step

a step of filling the heteropolyacid salt supported catalyst obtained in the first step, into a reactor for use in the reaction of the lower olefin with the lower aliphatic carboxylic acid in a gas phase;

Third Step

a step of contacting the heteropolyacid salt supported catalyst filled in the reactor, with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, in the absence of any lower olefin, and

Fourth Step

a step of passing a mixed gas containing the lower olefin and the lower aliphatic carboxylic acid through the heteropolyacid salt supported catalyst after the third step, to obtain the lower aliphatic carboxylic acid ester;

wherein the heteropolyacid salt is at least one salt selected from the group consisting of lithium salts, sodium salts, magnesium salts, barium salts, copper salts, gold salts and gallium salts of silicotungstic acid, phosphotungstic acid, phosphomolybdic acid, phosphovanadotungstic acid and phosphovanadomolybdic acid.

23. A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 39.7 to 46.3% by mass.

24. A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a silicon content of from 85 to 99% by mass in terms of silicon dioxide.

25. A siliceous support for use in a catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, which has a crush strength of 30 N or more.

26. A catalyst for producing a lower aliphatic carboxylic acid ester by reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase, comprising a support as claimed in any one of claims 23 to 25.

27. A catalyst according to claim 26, which has a crush strength of 30 N or more.

28. A catalyst according to claim 26, wherein at least one member selected from the group consisting of heteropolyacids and salts thereof is supported on the support.

29. A catalyst according to claim 28, wherein the heteropolyacids are selected from the group consisting of tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid, molybdosilicic acid, vanadotungstosilicic acid, vanadotungstophosphoric acid, vanadomolybdophosphoric acid, vanadomolybdosilicic acid, molybdotungstosilicic acid and molybdotungstophosphoric acid.

30. A catalyst according to claim 28, wherein the heteropolyacid salts are selected from the group consisting of lithium, sodium, magnesium, barium, copper, gold and gallium salts of tungstosilicic acid, tungstophosphoric acid, molybdophosphoric acid, molybdosilicic acid, vanadotungstosilicic acid, vanadotungstophosphoric acid, vanadomolybdophosphoric acid, vanadomolybdosilicic acid, molybdotungstosilicic acid and molybdotungstophosphoric acid.

31. A process for producing a catalyst comprising loading at least one member selected from the group consisting of heteropolyacids and salts thereof on a support as claimed in any one of claims 23 to 25.

32. A process for producing a catalyst comprising the following first and second steps:

First Step:

a step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on a support as claimed in any one of claims 23 to 25 to obtain a heteropolyacid and/or heteropolyacid salt-supported catalyst; and

Second Step:

a step of contacting the heteropolyacid and/or heteropolyacid salt-supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols to obtain a catalyst for producing a lower aliphatic carboxylic acid ester.

33. A process according to claim 32, wherein the gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols is a mixed gas of water and acetic acid.



34. A process for producing a lower aliphatic carboxylic acid ester, comprising reacting a lower olefin with a lower aliphatic carboxylic acid in a gas phase in the presence of a catalyst as claimed in claim 26.

35. A process according to claim 34, wherein the reaction of a lower olefin with a lower aliphatic carboxylic acid is carried out in the presence of water.

36. A process for producing a catalyst comprising the following first and second steps:

First Step:

a step of loading at least one member selected from the group consisting of heteropolyacids and salts thereof on a support as claimed in any one of claims 23 to 25 to obtain a heteropolyacid and/or heteropolyacid salt-supported catalyst; and

Second Step:

a step of contacting the heteropolyacid and/or heteropolyacid salt-supported catalyst obtained in the first step with a gas containing at least one member selected from the group consisting of water, lower aliphatic carboxylic acids and lower aliphatic alcohols, in the absence of any lower olefin, to obtain a catalyst for producing a lower aliphatic carboxylic acid ester.